



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

Note to Reader

Background: As part of its effort to involve the public in the implementation of the Food Quality Protection Act of 1996 (FQPA), which is designed to ensure that the United States continues to have the safest and most abundant food supply.

EPA is undertaking an effort to open public dockets on the organophosphate pesticides. These dockets will make available to all interested parties documents that were developed as part of the U.S. Environmental Protection Agency's process for making reregistration eligibility decisions and tolerance reassessments consistent with FQPA. The dockets include preliminary health assessments and, where available, ecological risk assessments conducted by EPA, rebuttals or corrections to the risk assessments submitted by chemical registrants, and the Agency's response to the registrants' submissions.

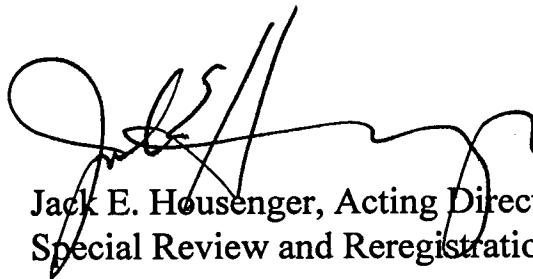
The analyses contained in this docket are preliminary in nature and represent the information available to EPA at the time they were prepared. Additional information may have been submitted to EPA which has not yet been incorporated into these analyses, and registrants or others may be developing relevant information. It's common and appropriate that new information and analyses will be used to revise and refine the evaluations contained in these dockets to make them more comprehensive and realistic. The Agency cautions against premature conclusions based on these preliminary assessments and against any use of information contained in these documents out of their full context. Throughout this process, If unacceptable risks are identified, EPA will act to reduce or eliminate the risks.

There is a 60 day comment period in which the public and all interested parties are invited to submit comments on the information in this docket. Comments should directly relate to this organophosphate and to the information and issues available in the information docket. Once the comment period closes, EPA will review all comments and revise the risk assessments, as necessary.

These preliminary risk assessments represent an early stage in the process by which EPA is evaluating the regulatory requirements applicable to existing pesticides. Through this opportunity for notice and comment, the Agency hopes to advance the openness and scientific soundness underpinning its decisions. This process is designed to assure that America continues to enjoy the safest and most abundant food supply. Through implementation of EPA's tolerance reassessment program under the Food Quality Protection Act, the food supply will become even safer. Leading health experts recommend that all people eat a wide variety of foods, including at least five servings of fruits and vegetables a day.

Note: This sheet is provided to help the reader understand how refined and developed the pesticide file is as of the date prepared, what if any changes have occurred recently, and what new information, if any, is expected to be included in the analysis before decisions are made. **It is not meant to be a summary of all current information regarding the chemical.** Rather, the sheet provides some context to better understand the substantive material in the docket (RED chapters, registrant rebuttals, Agency responses to rebuttals, etc.) for this pesticide.

Further, in some cases, differences may be noted between the RED chapters and the Agency's comprehensive reports on the hazard identification information and safety factors for all organophosphates. In these cases, information in the comprehensive reports is the most current and will, barring the submission of more data that the Agency finds useful, be used in the risk assessments.

A handwritten signature in black ink, appearing to read 'J. Housenger', is written over the typed name and title.

Jack E. Housenger, Acting Director
Special Review and Reregistration Division



**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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PESTICIDES AND TOXIC SUBSTANCES**

MEMORANDUM

RE: Water Resources Assessment for Diazinon

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DATE: May 10, 1999

This memorandum and the attachment represents the Water Resources Assessment for diazinon. It includes: (1) a summary of major conclusions describing the impact of diazinon use on the quality of ground and surface water resources, (2) a drinking water assessment describing the process used to estimate diazinon concentrations in drinking water, (3) a summary of the monitoring studies and (4) a summary of the

modeling results.

WATER RESOURCES ASSESSMENT

The purpose of this water resources assessment is to describe the occurrence of diazinon in water resources of the United States. This information on occurrence is used here to characterize the overall impacts on water quality from the use of diazinon, ecosystem exposure, and potential human exposure to diazinon via drinking water.

There are four major sections of this assessment. First, a summary of major conclusions describing the impact of diazinon use on the quality of ground and surface water resources. The summary is based on an evaluation of environmental fate data, monitoring studies conducted by state and federal agencies, modeling, and compliance information submitted to EPA from wastewater treatment facilities as a result of a permitting process. Second, there is a drinking water assessment describing the process used to estimate diazinon concentrations in drinking water, and uncertainties in our assessment. The third section describes individual monitoring studies and summarizes the results of each study. Monitoring was available to characterize the water quality impact of both agricultural and non-agricultural uses of diazinon (including urban uses, for example homeowner lawn care, pet groomers, kennels, and pest control businesses), and other non-agricultural uses, (for example forestry and rangeland uses); therefore, the monitoring studies are organized into these two categories with an additional category ("mixed") for studies of both agricultural and non-agricultural uses. Air, rain, and fog monitoring is also discussed. The fourth (and final) portion of this assessment summarizes and describes modeling results, which estimate concentrations that can occur in surface water as a result of diazinon use on specific agricultural crops. The modeling results are used to assess risk to aquatic species and are discussed in that context in the ecological risk assessment portion of this document. They have also been used, in part, to set the upper bound on the drinking water exposure estimate.

SUMMARY

The EPA's Office of Water has established an adult Lifetime Health Advisory (HAL) for diazinon of $0.6 \mu\text{g L}^{-1}$ but no Maximum Contaminant Level (MCL) has been established. Since drinking water facilities are not required to monitor for diazinon, only limited data were available to directly measure its concentration, or that of a major degradate oxyprymidine, in drinking water. The Office of Water also establishes criteria as

required by the Clean Water Act for the protection of aquatic life. The water quality criteria document for the protection of aquatic life from diazinon residues is in draft form at present, and are not described in this document.

Sources of monitoring data used in this assessment included: United States Geological Survey's (USGS) National Water Quality Assessment (NAWQA) (USGS, 1998) and National Stream Water Quality Network (NASQAN) (USGS, 1999) programs, the Permit Compliance System (PCS) database for National Pollutant Discharge Elimination System (NPDES) permits (USEPA, 1998), National Survey of Pesticide in Drinking Water (NPS) (USEPA, 1990), several states, and the open literature. The data reviewed in this assessment vary in quality, but are generally high overall, based on: QA/QC procedures, analytical methods, and field techniques. Contextual information on diazinon usage history in the areas monitored is, however, often quite limited.

Major Conclusions

Non-agricultural uses of diazinon, including homeowner uses, appear to have significantly affected both surface- and ground-water quality.

A major conclusion of USGS NAWQA program scientists is that urban use of diazinon has affected surface water quality in non-agricultural areas and is found more frequently and at higher concentrations in urban than in agricultural streams. Based on locations where ten or more samples were collected, 65.6% of surface-water samples in non-agricultural use-areas contained diazinon compared with 26.2% of the samples in agricultural areas (Table 7). While the peak concentrations reported were similar in non-agricultural and agricultural areas (2.90 and 3.80 µg/L, respectively), the 95th percentile concentration in the streams in non-agricultural areas was more than five times higher than in agricultural areas (0.28 µg/L and 0.052 µg/L, respectively). The NAWQA program limit of detection of diazinon is 0.002 µg/L.

In an analysis of pesticides in streams draining relatively small basins where pesticide use could be characterized as agricultural (40 streams) and urban (11 streams), NAWQA scientists reported that 16.9% of samples in agricultural areas, and 75% of samples in urban areas contained diazinon (Table 9). The 95th percentile concentrations at urban and agricultural sites were 0.43 µg/L (peak concentration of 1.9 µg/L) and 0.027 µg/L (peak concentration of 1.2 µg/L), respectively. NAWQA scientists noted that a distinctive feature of urban streams was the common occurrence of mixtures of both herbicides and insecticides. More than 10 percent of the urban stream samples contained a mixture of at least four herbicides plus diazinon and chlorpyrifos.

The following are examples of diazinon impacts on urban surface-water quality in

several states:

- **California: Castro Valley Creek Watershed:** A study was conducted during the 1995-96 and 1996-97 rainy seasons (October - May) in the Castro Valley Creek watershed to determine the temporal and spatial variability of diazinon in surface water and the sources of diazinon in the watershed. Land use in this relatively large urban watershed was 50% residential and 15% commercial (35% undeveloped). Diazinon concentrations streams in the watershed appeared to peak in the spring and fall and, therefore, correlated with application patterns in urban areas. The largest diazinon detections occurred in runoff following extended dry periods. Diazinon was detected in *all* of the 42 samples collected near the mouth of Castro Valley Creek in the two years of monitoring (Table 17). A second study of the Castro Valley Creek watershed (Table 18) was conducted to evaluate diazinon impacts in subcatchments. Monitoring at the discharge points of each subcatchment, indicated that those with the largest areas of undeveloped land had the smallest diazinon concentrations. In this study, roughly 80% of the samples collected in each subcatchment contained diazinon.
- **California: three residential sites:** In the Castro Valley Creek watershed and in Oakland a residential runoff study was conducted to determine the concentrations of diazinon in rainfall and runoff resulting from ant control treatments. Water samples were collected from gutters, patios, roof drains, driveways, and rainfall at three residential sites. Diazinon was detected in 100% of the samples, and was found as long as seven weeks after application. Concentrations in the rainfall itself ranged up to 1.3 µg/L; in the other samples of runoff collected adjacent to treated areas, diazinon concentrations were reported up to 1,200 µg/L (Table 19). In this study, diazinon was applied at 2/3 the normal application rate for ant control; thus, the reported concentrations resulted from this reduced application rate.
- **Colorado:** A study conducted in Colorado confirms the NAWQA findings that urban uses tend to have higher frequencies of detection of diazinon than agricultural uses. Diazinon was detected more often in urban surface water samples (72%) than in agricultural surface water samples (24%), as shown in Table 13. Higher concentrations were measured in the May through September time-period.
- **Washington:** In King County, Washington, a recent study conducted in April and May of 1998 showed that diazinon was detected in nine out of 10 urban streams. Although these samples do not represent a long-term concentration, diazinon concentrations in all but one of the streams exceeded California standards for long-term exposure of aquatic life. Concentrations ranged up to 0.425 µg/L. All of the detections are believed to be linked to homeowner lawn

care practices.

A total of 3,023 ground-water sites (each site sampled once) were analyzed by the US Geological Survey's (USGS) National Water Quality Assessment (NAWQA) program from both agricultural and non-agricultural sites. Overall, 1.69% of the ground-water samples contained diazinon. As seen in Table 3, diazinon was found more often in shallow ground water (less than 10 years old) in urban areas than agricultural settings, reported in 1.66% versus 0.5%. The magnitude of the concentrations was low overall with a maximum concentration of 0.077 µg/L in agricultural areas and 0.01 µg/L in urban areas.

Monitoring data indicate widespread occurrence of diazinon in surface water nationally.

Diazinon was the most frequently detected insecticide in surface water in the NAWQA program. Diazinon has been measured in surface water in 24 states plus Washington, DC. In addition, wastewater treatment facilities in 14 states (six additional states) have reported high concentrations of diazinon in effluent discharged to surface water.

A total of 1,058 surface water sites and 5,155 samples were analyzed by the US Geological Survey's (USGS) National Water Quality Assessment (NAWQA) program from both agricultural and non-agricultural sites. Though the NAWQA program did not specifically target diazinon use areas, 35% of the surface water samples collected contained diazinon, with a peak concentration of 3.8 µg/L (Table 6). In an analysis of a subset of data NAWQA believed to best represent land use, three out of four samples from urban streams contained diazinon residues. As part of this analysis, NAWQA collected samples at 14 "integrator" sites from large streams and rivers that drain relatively large basins in which pesticide use, soils, and land use are heterogeneous. NAWQA scientists reported that 45% of samples, or almost one out of every two samples contained diazinon (Table 10) at concentrations up to 0.40 µg/L. The 95th percentile concentration calculated by NAWQA was 0.073 µg/L.

Diazinon was detected in every major river basin, including the Mississippi, Columbia, Rio Grande, and Colorado, in the USGS NASQAN study (Table 11) diazinon was detected in 33% and 26% of the samples from the Rio Grande and Mississippi rivers. These rivers drain a significant portion of the US. The limit of detection for diazinon in the NASQAN study was 0.002 µg/L.

Diazinon is widely used in California and, for this reason, a great deal of surface water monitoring has been conducted by several agencies from 1992 to 1998. To date, diazinon has been detected in the San Joaquin River, the Sacramento River, the Merced River, Russian River, the Tuolumne River, Orestimba Creek, and the

Stanislaus River.

Diazinon residues have been found in large rivers and major aquifers.

Major rivers: The USGS National Stream Water Quality Network (NASQAN) program monitors water quality in the Nation's largest river basins. Diazinon was detected (1995-1998) in all of the major rivers in NASQAN including the Rio Grande, Mississippi, Columbia, and Colorado and in 33%, 26%, 7%, and 7% of the samples, respectively. From hundreds of samples collected (Table 11), concentrations ranged up to 0.207 µg/L using a detection limit of 0.002 µg/L. That diazinon is found in these large rivers is extremely important. Because the volume of water flowing in these rivers is very large, the low pesticide concentrations reported result in a high total mass of diazinon transported in these rivers.

It is significant that NAWQA data confirm the NASQAN findings for large streams and rivers. In an analysis of a subset of data NAWQA believed to best represent land use, NAWQA collected samples at 14 "integrator" sites from large streams and rivers that drain relatively large basins in which pesticide use, soils, and land use are heterogeneous. NAWQA scientists reported that 45% of samples, or almost one out of every two samples contained diazinon (Table 10) at concentrations up to 0.40 µg/L. The 95th percentile concentration calculated by NAWQA was 0.073 µg/L.

Major aquifers: Data from the USGS NAWQA program reported a 1.82% detection frequency of diazinon in major aquifers, with a maximum concentration of 0.085 µg/L. Major aquifers are defined as those that are major current or future sources of ground water supply within a specific hydrogeologic region. Samples are collected from these aquifers from large drinking water supply wells (production wells) (Table 4). Among the set of pesticides that NAWQA looked at, diazinon is one of the two insecticides found in these major aquifers (the other is carbaryl). All of the other pesticides found were herbicides (10 of them including atrazine and its degradation product deethylatrazine (DEA), metolachlor, cyanazine, alachlor, bentazon, simazine, prometon, diuron, and tebuthiuron). While there was a low rate of false positives for diazinon in the ground-water program (see NAWQA ground water summary below), the number of detects is substantially more than could be accounted for by the false positive rate.

Diazinon was detected in drinking water wells in Missouri (1987-88), Mississippi (1983-84), Virginia (1989-90) (Tables 20, 21, 22). In all three of these states, the detections occurred in wells located in agricultural areas. Diazinon residues were found in deep wells in both Missouri (average of 81 feet) and Virginia (average of 200 feet), indicating that residues may be transported to relatively deep ground water. The highest concentration seen in these wells was 1.00 µg/L.

Many wastewater treatment facilities in 14 states are out of compliance with the Clean Water Act as a result of diazinon residues in effluent.

All facilities where water is discharged directly into surface waters must obtain a permit through the National Pollutant Discharge Elimination System (NPDES) to be in compliance with the Clean Water Act. The EPA's Office of Water is presently writing the water quality criteria document for the protection of aquatic life from diazinon residues. Both acute and chronic protection limits for fresh and saltwater species are being developed. The acute number are almost final but there is a additional work needs to be done for the chronic numbers.

The EPA's Permit Compliance System (PCS) is a national database of NPDES data that tracks permit issuance, permit limits, and monitoring data for over 64,000 regulated facilities. Toxicity tests conducted at 16 of these facilities failed because of the presence of diazinon. Diazinon was detected in 52% of the influent samples and 40% of the effluent samples from these facilities between 1994 and 1998. Maximum concentrations were 11.0 µg/L and 10.0 µg/L for the influent and effluent samples, respectively (Table 14).

A nationwide survey, conducted by the National Effluent Toxicity Assessment Center (NETAC) to determine the occurrence of diazinon in the effluent from wastewater treatment facilities (sometimes referred to as publicly owned treatment works or POTWs) showed that 65% of the samples contained diazinon residues (Table 15).

A total of 47 facilities across the US have failed toxicity tests because of diazinon in their effluent. Below are examples of monitoring at wastewater treatment facilities in several states:

- **Texas.** Diazinon has caused wastewater treatment facilities to fail toxicity tests in eight large municipal systems including the Cibolo Creek Municipal Authority (City of Denton), City of Big Spring, City of Greenville, City of Fort Worth, City of Temple, City of Tyler, and the Trinity River Authority.
- **California.** In 1996, The California EPA and the Contra Costa Sanitary District conducted a study in Contra Costa, Alameda, and Santa Clara counties, California to determine the load of diazinon and chlorpyrifos in wastewater in residential areas, at commercial sites, and in influent to three wastewater treatment facilities. Diazinon was detected in 83% of the samples from the residential areas (constituting 82% of the load to the treatment facility) at concentrations up to 4.30 µg/l. The detection limit of diazinon was 0.05 µg/l. Diazinon was detected in 53% of the samples from nine of the 12 commercial sites tested, which included pet groomers, kennels, and pest control businesses. The largest diazinon concentration of 20.0 µg/L was detected in the wastewater

from a kennel. Diazinon was detected in 100% of the samples from all three treatment plants at concentrations ranging from 0.066 to 0.940 µg/L (Table 16).

- **Florida.** Diazinon use by professional lawn care applicators (approximately 200,000 pounds) is higher in Florida than anywhere else in the US. In Florida, whole effluent testing is done for wastewater treatment facilities to detect toxicity from a mixture of chemicals, including diazinon. Concern for diazinon in effluent from these facilities occurred as early as 1988; however, within the past five years the State has recognized an increasing occurrence of diazinon-related toxicity in analyses of effluent. To date, diazinon has been detected in approximately 21 facilities at concentrations ranging up to 1.57 µg/L.
- **Oklahoma.** Four large wastewater treatment facilities have consistently failed toxicity tests from 1996 to 1998. The Oklahoma Department of Environmental Quality (DEP) believes that spring and summer lawncare applications are the cause of the diazinon residues in the wastewater. Because of these failures, USEPA's Region 6 required the facilities to conduct an educational campaign on diazinon use. Oklahoma does not treat their effluent to remove diazinon because it is too costly.

Diazinon has been measured in air, rain, and fog.

Diazinon is the most common organophosphate compound detected in air, rain, and fog (followed by methyl parathion, parathion, Malathion, chlorpyrifos, and methidathion). In the 1970's, diazinon was detected throughout the US. Since then, most sampling and analyses have been done in California fog and air.

Air. In 1971, diazinon was detected in approximately 80% of the sites sampled nationally. Over 60% of these sites also contained diazinon OA. By 1988, sampling was done only in California. Diazinon and diazinon OA were detected in approximately 90% and 85% of the sites sampled. A 1976 study indicated that there was a strong correlation between high air concentrations, regional use, and cropping patterns. Concentrations of diazinon in air range from 0.0011 to 306.5 ng/cubic meter; for diazinon-OA they range from 0.0014 to 10.8 ng/cubic meter.

Recent USGS monitoring also indicates that diazinon is being found in Sacramento urban air samples as well as samples taken in agricultural areas upwind and downwind of the urban site. The USGS conducted a study to monitor the occurrence, concentration, and geographical distribution of agricultural pesticides in air over the Mississippi River. Diazinon was detected in all of the samples (100%) at concentrations ranging from 0.04 to 0.36 ng/m³. The highest concentrations of diazinon, chlorpyrifos, and malathion were observed near major metropolitan areas where agricultural use of these chemicals was minimal.

Rain. Rain has not been analyzed for pesticides as often or at as many sites as air. Concentrations of diazinon in rain ranged from 1.3 to 2,000 ng/L; for diazinon-OA they ranged from 1.3 to 115.8 ng/L (Majewski and Capel, 1995). More recent monitoring (April-September 1995) has been conducted by the USGS in the Mississippi River valley. Five insecticides, including diazinon, were frequently detected. In two of the three urban sites, significantly more diazinon was detected in the rainfall than at the agricultural sites.

Fog. Of the 48 pesticides that have been detected in fog, only diazinon was near or exceeded the human health limits for drinking water in 5 of 24 fog events (Majewski and Capel, 1995). Concentrations of diazinon in fog were measured as high as 76,300 ng/L; for diazinon-OA they range up to 28,000 ng/L.

Environmental fate data predicted that water contamination would occur from diazinon use.

The environmental fate characteristics of diazinon suggest that it will occur in both ground and surface water to varying degrees. Diazinon is only moderately mobile (K_d s range from 3.7 to 11.7) and is persistent (aerobic soil metabolism half-life of 38 days). Laboratory data also suggest that diazinon will not persist in acidic waters. However, in neutral and alkaline waters residues are quite persistent.

Laboratory data indicate that oxypyrimidine (G-27550), a major degradate of diazinon, is likely to leach in vulnerable environments and would probably be found in ground water at much higher levels than parent diazinon. No monitoring information is available for this major diazinon degradate.

Dormant spray use of diazinon has resulted in surface-water contamination in California.

Diazinon is applied as a dormant spray to orchard crops in California's Central Valley. Several studies have shown that diazinon is not detected in any of the surface water samples collected prior to application (which usually occurs during the winter). However, despite lower than normal application rates, diazinon has consistently been detected in several creeks and rivers in the Sacramento River watershed and the San Joaquin River watershed during the winter rainy season. Diazinon was detected during the winters after application occurred from 1991 through 1998. Diazinon was detected in 5% to 100% of the samples from a variety of locations using diazinon as a dormant spray. Concentrations were very high and ranged up to 36.8 µg/L. A USGS study also concluded that diazinon was found in urban storm runoff because of applications of dormant agricultural sprays in Modesto, California (Tables 12, 23, 26-31).

Lack of good usage data, especially for non-agricultural uses, makes it difficult to know the real impact of diazinon use on water resources.

The diazinon use information is incomplete (especially non-agricultural use) and at too coarse a scale to identify potentially exposed populations with any certainty. If this information was available, vulnerable drinking water sources could be identified. Surface and ground water residues could be significantly higher than in data currently available if monitoring was targeted to those areas where high diazinon usage is known to occur.

Targeting water monitoring in diazinon use areas is especially difficult because of its fragmented use pattern. Major agricultural crops tend to be treated with diazinon only occasionally; non-agricultural use is primarily by very small users and is largely undocumented. Despite the fact that none of the studies reviewed in this assessment were targeted to diazinon use areas, diazinon was still detected in surface water in surprising frequency.

Very few data are available that directly measure diazinon (or the degradate oxypyrimidine) concentrations in drinking water or in reservoirs.

EPA has not established an MCL for diazinon or oxypyrimidine; thus, water supply utilities nationwide have not routinely analyzed drinking water for diazinon. Few reservoir monitoring studies have been conducted; where results are available, studies have focused on a small suite of analytes, usually herbicides. EFED is not aware of any monitoring data in reservoirs where diazinon was an analyte.

Laboratory data indicate that oxypyrimidine (G-27550), a major degradate of diazinon, is likely to leach in vulnerable environments. Recent monitoring information indicates that the overall occurrence and concentrations of pesticides in ground water is often greatly underestimated when the pesticide degradates are not evaluated in addition to parent compounds. No monitoring information is available for this major diazinon degradate.

Monitoring studies must be carefully designed in relation to pesticide application and runoff events in order to adequately characterize occurrence.

The concentrations of diazinon found in surface water are directly related to the frequency and timing of monitoring in relation to pesticide application and storm runoff events. This is demonstrated by numerous studies that have been conducted in the

Central Valley of California, particularly those that characterize the impact of diazinon used as a dormant spray. Diazinon was not detected pre-application, but was correlated with rainfall events. The frequency and concentration of diazinon may have been reduced as a result the sampling design as by well as flood events. Studies that demonstrate this include: Sacramento River Watershed (1996-7) and (1997-8); San Joaquin watershed 1997 and 1998. Future monitoring study designs must take this into account in order to accurately assess acute, short-term exposure.

DRINKING WATER EXPOSURE ASSESSMENT

Using monitoring and modeling data, acute and chronic concentrations of diazinon in drinking water were estimated for both surface water and ground water. Since more monitoring information is available for surface water, it was possible to estimate concentrations in both agricultural and non-agricultural use areas. For surface water, a range of values is presented with the lower end of the range derived from monitoring data and the upper end of the range derived from modeling data. The lower end of this range represents the *minimum* exposure expected; the upper end of the range represents the maximum exposure estimated from modeling. Because of limited diazinon use data, especially for non-agricultural uses, diazinon exposure is likely to be higher in some areas than is indicated by the monitoring data. There is also uncertainty in the model estimates, as the models used have not been field validated.

Acute concentrations of diazinon in drinking water

Surface Water. Acute concentrations of diazinon in surface water are presented as a range of values rather than a discrete value. The lower concentration was derived from monitoring data; the upper concentration was derived from modeling. Monitoring data underestimates the peak exposure because of the following sources of uncertainty:

- The percentage of each county (Merced, Sacramento, San Joaquin, Stanislaus) treated with diazinon in the sampled watersheds during the majority of the sampling periods (dormant spray period: December thru March) was estimated to be less than one percent.
- There is a lack of monitoring data in the majority of diazinon use areas (both agricultural and non-agricultural).
- The concentrations of diazinon found in surface water are directly related to the frequency and timing of monitoring in relation to pesticide application and runoff events.

Monitoring: There were 98 agricultural and 26 non-agricultural sites where samples

were collected from surface waters that were potential drinking water sources (rivers, streams, etc.). The maximum measured value of the diazinon concentration was recorded at each monitoring site. The lower bound on acute exposure was estimated by aggregating the maximum values measured in each study (separating out agricultural and non-agricultural studies), and using the 95th percentile value.

Modeling: Because of the uncertainties noted above, we estimated an upper bound acute exposure value from the modeling data. Since we had monitoring data from an area (the San Joaquin and Sacramento River Watersheds in California) where diazinon was used on dormant spray crops (for example almonds and walnuts) and the use rate on these crops in this area is very high, we selected similar modeling scenarios. PRZM/EXAMS modeling was done for walnuts and almonds in the Central valley of California. The one-in-ten-year peak value (or 90th percentile value) for the two crops grown in this area was 22 $\mu\text{g L}^{-1}$ (walnuts). The same value (22 $\mu\text{g L}^{-1}$) was used for the non-agricultural use upper bound acute exposure value for two reasons: (1) because we do not have the tools to model non-agricultural use exposure and (2) the results of modeling for this agricultural use are likely to provide a conservative estimate of the non-agricultural upper bound acute exposure as a result of the heavier non-agricultural loading to the watershed. There are two pieces of information that support this. USGS NAWQA data (for locations with ten or greater samples) show that the percent detects from non-agricultural use areas was 65.6% and that from agricultural use areas was 26.2%. Second, the non agricultural use of diazinon constitutes roughly three-quarters of the overall diazinon use. There is still a significant potential for underestimation of maximum acute exposure to diazinon from surface water drinking water sources because of the limited monitoring and usage data, especially in non-agricultural use areas.

Groundwater: Acute concentrations of diazinon in ground water are presented as a discrete value, because, although significant uncertainties exist in monitoring data, acceptable modeling tools are not yet available. The acute diazinon concentration in groundwater has a high degree of uncertainty in capturing the maximum exposure to diazinon from groundwater drinking water sources because of the lack of monitoring data in the majority of diazinon use areas and the lack of modeling data to place an upper bound on the potential exposure.

Monitoring: The monitoring data for groundwater is much more limited than for surface water. There are only three studies other than the USGS NAWQA data. All the studies were from agricultural use areas except a fraction of the USGS NAWQA data. The NAWQA groundwater data had 0.7% detects in the field blanks spiked with diazinon and the total percent of detects for the environmental samples was 1.7. Even with this limited data set the acute exposure value calculated from the 95th percentile of the maximum values (same method as for the surface water) is greater than the value estimated using the screening model, SCI-GROW (0.804 $\mu\text{g L}^{-1}$). Since there is no

approved Tier II model for estimating groundwater concentrations at this time, the 95th percentile of the maximum values is used to represent both the maximum and minimum concentrations in groundwater.

Chronic concentrations of diazinon in drinking water

Surface Water: The 95th percentile of the arithmetic means of all samples at each site (detects and non-detects) from monitoring studies whose samples were from potential drinking water sources was used for the lower bound chronic concentration. Samples with values below the LOD were given a value of one-half the LOD. The same logic was used to calculate the upper bound chronic concentration as was used for the upper bound acute concentration (described in the surface water acute section above). Providing an upper and lower chronic concentration from the available monitoring and modeling data reduces the uncertainty somewhat, but the lack of monitoring data in the majority of the diazinon use areas still means that the maximum chronic concentration may be greater than the estimated value.

Groundwater: The chronic concentration estimate for groundwater was the same as that used for the acute estimate. Groundwater velocity is small compared to surface water and physicochemical processes result in pesticide plumes that can potentially have relatively uniform concentrations. Concentrations measured at a well may show only small fluctuations in concentration especially as the sampling point distance from the pollution source increases. Again, this estimate may not be representative of actual maximum chronic concentrations because of the limited data set and the lack of an upper bound estimate from Tier II modeling data.

Table 1. Estimated diazinon exposure ($\mu\text{g L}^{-1}$) in drinking water		
Type	Acute	Chronic
Surface Water		
Agricultural Use	2.3 -22	0.19 -5.8
Non-Agricultural Use	3.0 -22	0.46 -5.8
Ground Water	0.90	0.90

MONITORING STUDY SUMMARIES

This section describes individual monitoring studies and summarizes the results of each study. Monitoring was available to characterize the water quality impact of both agricultural and non-agricultural uses of diazinon (including urban uses, for example homeowner lawn care, pet groomers, kennels, and pest control businesses), and other non-agricultural uses, (for example forestry and rangeland uses); therefore, the monitoring studies are organized into these two categories with an additional category

(“mixed”) for studies of both agricultural and non-agricultural uses. Substantially more monitoring data were available for surface-water than for ground-water resources.

Data Sources and Considerations

There is a range of sources for diazinon monitoring information with variable data quality. Sources used in this assessment included: United States Geological Survey’s (USGS) National Water Quality Assessment (NAWQA) (USGS, 1998) and National Stream Water Quality Network (NASQAN) (USGS, 1999) programs, the Permit Compliance System (PCS) database for National Pollutant Discharge Elimination System (NPDES) permits (USEPA, 1998), National Survey of Pesticide in Drinking Water (NPS) (USEPA, 1990), several states, and the open literature.

When reviewing the data the following should be considered:

- All of the data are from studies that did not specifically target diazinon as a contaminant. Therefore, these studies do not directly relate diazinon use with concentrations in surface water or ground water.
- The amount of background and site characterization information varied greatly between studies. This information is critical in determining the relevance of the study results to human exposure to diazinon in drinking water.
- The limit of detection (LOD) for the analytical techniques used to quantify diazinon concentrations in the monitoring samples varied between studies. This directly impacts detection frequencies and should be considered when comparing the results from different studies.

MIXED USE MONITORING STUDY SUMMARIES

US Geological Survey’s National Water Quality Assessment Program (NAQWA).

The NAWQA program was designed to describe the status and trends of a representative portion of the nation’s water quality and to provide a sound scientific understanding of the primary natural and human factors affecting the water quality (Hirsch et al., 1988). The NAWQA program is an aggregation of some 60 regional study units, which are monitored on a rotating schedule to take into account long-term variations in water quality. NAWQA study units are geographically defined by a combination of ground- and surface-water features and usually encompass more than 10,000 square kilometers.

The USGS Pesticide National Synthesis Project provides the following considerations for data interpretation:

The NAWQA program is based on a complex sampling design that targets specific land use and hydrologic conditions in addition to assessing the most important aquifers and streams in each area studied. Although studies in each NAWQA study unit have some common design elements, they are not specifically designed to produce a statistically representative analysis of national water-quality conditions, especially with results only from the first 20 study units.

For both streams and ground water, a major component of the sampling design is to target specific watersheds and shallow ground water areas that are influenced primarily by a single dominant land use (agricultural or urban) that is important in the particular area. This component of the design facilitates the summary of results by agricultural and urban land use settings, but results require careful interpretation.

The NAWQA design does not result in an unbiased representation of all streams or shallow groundwater in agricultural settings. For agricultural land use, the focus was limited to the most important agricultural settings within the first 20 study units. Thus, some agricultural activities and related pesticide use that may be very important in a particular part of the nation are not included. For example, the 20 study areas did not include intensive rice growing areas. On the other hand, a particular pesticide may be important in one or two of the 20 study units, but not in the others, and the averaged results may be misleading in this regard. Another possibility is that use of a particular pesticide is much greater than average in the watersheds and groundwater areas studied, leading to an overestimate of occurrence and concentrations relative to other areas. Similar biases are possible for urban areas as well, but the dominant pesticides used are probably more similar among urban areas than they are among agricultural areas with different crops.

For both streams and groundwater, statistical summaries for “agricultural” and “urban” land uses and for “major streams” and “major aquifers” were prepared by the USGS from a carefully selected subset of the complete NAWQA data set in order to control or minimize biases due to different temporal sampling strategies and special studies. They state that “The summaries are designed to give a broad and averaged perspective on national results.” The criteria for data selection are described below for ground water and surface water, separately.

Although the quality of the NAWQA data is excellent, the program was not designed to target diazinon (or other pesticide) use areas and, therefore, the overlap between the NAWQA sampling sites and use areas for diazinon is largely unknown (Figures 1 and 2). NAWQA data are available via the Internet at <http://water.wr.usgs.gov/pnsp/allsum/>.

Ground Water

The USGS generated statistical summaries of the ground-water data for three different settings: shallow ground water in primarily agricultural areas (Table 3), shallow ground water in primarily urban areas (Table 3), and major aquifers (Table 4). The agricultural and urban land-use categories were represented by wells chosen or designed to sample shallow, recently recharged ground water to determine the effects of specific land uses on water quality. Sites comprising the “major aquifer” category had no such restrictions on land use or water age, and thus, represent a broader mixture of land uses and ground water depths.

Table 2 summarizes data for every NAWQA ground-water sample that was analyzed for pesticides, including newly drilled monitoring wells, production wells (such as domestic and public-supply wells), springs, and tile drains. Although Table 2 provides a complete summary of all NAWQA results, it should not be presumed to be a statistically representative summary of the NAWQA pesticide results. The data in the table contain a variety of spatial and temporal biases for which corrections must be applied before any reliable statistical summaries can be compiled. For example, many of the sites were sampled more than once for pesticides. Failure to account for this would lead to an over-representation of these sites in any statistical summary of chemistry data in which they were included.

The USGS followed the following procedures to generate the relatively unbiased and comparable statistical summaries using data from NAWQA ground-water sampling networks presented in Tables 2 and 3:

- (1) Tile drains and springs were excluded to reduce the variability in site type.
- (2) Any well co-located with another existing well was excluded (to examine the effects of well depth or well type, for example). Thus, the networks albelus2, gaillusur3b, sanjlus42, sanjlus52, sanjlus62, trinusur2, and trinusur3 were excluded.
- (3) Networks with fewer than 10 wells were excluded because they contained an insufficient number of wells to be spatially representative of an area.
- (4) Wells that were included in more than one type of network (e.g. a land-use study and an aquifer survey) were allowed to exist in both.
- (5) One sample from each well was selected. Generally this was the first sample collected.

Samples were collected between 6/30/92 and 11/15/96. The LOD for diazinon was $0.002 \mu\text{g L}^{-1}$. No degradates were analyzed.

Table 2. Results ($\mu\text{g L}^{-1}$) from the USGS NAWQA monitoring program for all wells sampled						
Wells	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
2616	3023	51	0.160 - ND ²	0.014	ND	ND

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

Table 3. Results ($\mu\text{g L}^{-1}$) from the USGS NAWQA monitoring program for shallow ground water							
Land Use	Wells	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
Urban	301	301	5	0.010 - ND ²	NR ³	ND	NR
Agricultural	924	924	5	0.077 - ND	NR	ND	NR

¹ Range and 95th percentile are determined from all samples.

² Below the LOD.

³ Not Reported.

Table 4. Results ($\mu\text{g L}^{-1}$) from the USGS NAWQA ground-water monitoring program for major aquifers.						
Wells	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
933	933	17	0.085 - ND ²	NR ³	ND	NR

¹ Range and 95th percentile are determined from all samples.

² Below the LOD.

³ Not Reported.

Surface Water

Table 5 summarizes results from all NAWQA sites where streams were sampled for pesticides. These include sites sampled many times over several years, as well as sites sampled only once or twice. The results summarized in Table 5 are from all stream samples, including samples collected on a fixed sampling frequency, high flow samples, low flow samples, diurnal and storm hydrograph samples, and samples collected as part of special synoptic studies. Because all sites and all samples are included, the summary statistics shown in Table 5 are likely to be biased. For most compounds, the detection frequencies and concentration percentiles shown will be biased high for commonly occurring conditions because more samples were collected at sites where concentrations were high, or samples were collected more frequently during periods of elevated concentrations. For some compounds, on the other hand, the values shown may be biased low because sampling was not conducted during high-use periods. The maximum concentrations shown in Table 5 are the highest concentrations observed in all NAWQA stream samples. Table 5 should not be

presumed to be a statistically representative summary of the NAWQA pesticide results. Samples were collected between 4/20/92 and 12/16/96. The LOD for diazinon was $0.002 \mu\text{g L}^{-1}$.

Table 5. Results ($\mu\text{g L}^{-1}$) from the USGS NAWQA surface water monitoring program.							
Land Use	Sites	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
Agricultural	507	2977	703	3.80 - ND ²	0.017	0.042	ND
Non-Agricultural	551	2178	1095	2.90 - ND	0.050	0.240	0.003

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

Table 6. Results ($\mu\text{g L}^{-1}$) from the USGS NAWQA surface water monitoring program for agricultural land use monitoring sites where pesticides are used.						
Sites	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
381	1989	544	3.80 - ND ²	0.023	0.075	ND

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

We selected a subset of the NAWQA surface water data for analysis using only sites at which at least ten samples were collected. Because of the high temporal variability of surface water concentrations, it was felt that this dataset would more accurately represent pesticide concentrations in surface water. These data are presented in Table 7.

Table 7. Results ($\mu\text{g L}^{-1}$) from the USGS NAWQA surface water monitoring program for sites with ten or more samples.							
Land Use	Sites	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
Agricultural	59	2183	572	3.80 - ND ²	0.019	0.052	ND
Non-Agricultural	31	1161	762	2.90 - ND	0.065	0.280	0.011

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

Linear regression was used to relate the concentration results for sites with ten or more samples to pesticide use for the period 1992-97, and to several physicochemical parameters of the sampled surface waters. There were 36 sites that had agricultural

land use classifications and diazinon use. Separate regressions were calculated for each predictor (independent variable). The table below gives the p-value and r^2 for each predictor. These statistics can be interpreted as follows: r^2 gives the proportion of variance of concentration explained by a linear relationship with a given predictor. The value of r^2 will be between zero and 1, with larger values indicating more variability explained. The p-value is used to assess whether or not an apparent relationship (as measured by r^2 or the regression slope) can be attributed to variability in the data (Table 8).

According to the conventional criterion of statistical significance (p-value at or below 0.05), none of the regressions are significant except for the relationships with specific conductivity and dissolved oxygen. For both regressions the slopes were negative. However, the low value of r^2 indicates that the relationship is weak in terms of the fraction of variation in concentration that can be explained by variation in specific conductivity or dissolved oxygen.

Table 8. Results from the regression analysis of diazinon concentration against (1992-97) diazinon use and physicochemical parameters of the sampled surface waters.¹		
Regressed Parameters	r^2	p-value
Diazinon Conc. vs Use	0.014	0.49
Diazinon Conc. vs pH	0.018	0.44
Diazinon Conc. vs Streamflow	7.4×10^{-4}	0.87
Diazinon Conc. vs Temp.	9.7×10^{-3}	0.57
Diazinon Conc. vs Specific Conductivity	0.41	2.7×10^{-5}
Diazinon Conc. vs Dissolved Oxygen	0.31	4.7×10^{-4}

¹ All regressions calculated using mean values. Non-detects were given a value of one-half the LOD. Agricultural use data for 1992-1997 from Doanes Marketing Research, Inc.

USGS scientists identified several subsets of sampling locations they believe to characterize agricultural, urban, and mixed land uses. Tables 9 and 10 summarize the results of NAWQA sampling for pesticides in streams draining relatively homogenous basins that represent specific agricultural and urban land uses (indicator sites) and streams draining large basins with mixed land uses (integrator sites). The summaries in Tables 9 and 10 are based on samples collected during a one-year period at 65 sites located on streams within the first 20 NAWQA study units. Table 9 summarizes results from 40 streams with primarily agricultural basins. These agricultural indicator sites have relatively small basins (27 to 6000 sq km, with most less than 1000 sq km) and include a variety of different crop types and agricultural practices. Table 17 summarizes results from 11 streams with primarily urban basins. These urban indicator sites have small basins (25 to 108 sq km) in which the primary uses of pesticides are non-agricultural. Table 10 summarizes results from 14 integrator sites on large streams

and rivers that drain relatively large basins (1800 to 92000 sq km) with heterogeneous land use, diverse soil types and topography, and usually a variety of pesticide uses. Samples were collected throughout the year at most of the 65 sites included in Tables 9 and 10.

Not all samples collected during the year at each site were used in the USGS calculation of the summary statistics, however. Samples collected as part of a fixed-frequency sampling schedule were included, along with a much smaller number of samples collected during selected high or low flow conditions. Samples collected over a storm hydrograph, or as part of a study of diurnal variability, were excluded in order to avoid bias resulting from repeated sampling during extreme conditions. The sampling frequency at most sites was higher during periods of the year when pesticide concentrations were expected to be elevated, so that the detection frequencies and concentration data shown may be somewhat higher than would be obtained from samples evenly distributed throughout the year. At most sites, 1 to 2 samples were collected each month during periods when pesticide transport in the streams was expected to be low. Sampling frequency increased to 1 to 3 samples per week during periods when elevated levels of pesticides were expected in the streams.

Table 9. Results ($\mu\text{g L}^{-1}$) from the USGS NAWQA surface water monitoring program for 40 agricultural and 11 urban sites.							
Land Use	Sites	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
Urban	11	326	244	1.90 - ND ²	NR ³	0.430	NR
Agricultural	40	1000	169	1.20 - ND	NR	0.027	NR

¹ Range and 95th percentile are determined from all samples.

² Below the LOD.

³ Not Reported.

Table 10. Results ($\mu\text{g L}^{-1}$) from the USGS NAWQA surface water monitoring program for 14 integrator sites on large streams and rivers.						
Sites	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
14	245	111	0.40 - ND ²	NR ³	0.073	NR

¹ Range and 95th percentile are determined from all samples.

² Below the LOD.

³ Not Reported.

USGS National Stream Water Quality Network (NASQAN). The NASQAN program monitors water quality in the Nation's largest river basins including the Rio Grande, Colorado, Columbia and Mississippi. The program design is such that it cannot address local water quality conditions along the major rivers but it can assess regional variability. The data reported are from January 1, 1995 to September 30, 1998. The

LOD for diazinon was 0.002 µg/L.

Diazinon has been detected in all of the major rivers in NASQAN. In the Rio Grande, Mississippi, Columbia, and Colorado rivers, diazinon was detected in 33%, 26%, 7%, and 7% of the samples, respectively. Concentrations ranged up to 0.207 µg/L (see Table 11 for mean, median, and 95th percentile).

Finding diazinon in these large rivers is extremely important. Since the volume of water flowing in these rivers is very large, any pesticide found in the river will be significantly diluted. Therefore, the total mass of diazinon in these rivers is very high.

Table 11. Results from the USGS NASQAN surface water monitoring program.							
River Basin	Sites	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
Rio Grande	6	193	64	0.207 - ND ²	0.011	0.055	ND
Mississippi	23	794	203	0.102 - ND	0.003	0.011	ND
Columbia	7	228	16	0.009 - ND	ND	0.003	ND
Colorado	9	162	12	0.008 - ND	ND	0.004	ND

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

National Survey of Pesticide in Drinking Water (NPS). The EPA's NPS was designed to determine the frequency of pesticide and nitrate-nitrogen contamination in ground water by sampling community water systems and rural drinking water wells nationwide. A total of 1,349 wells (783 rural domestic wells and 566 community water system wells) were randomly selected and sampled once for diazinon (parent only) in 38 states (USEPA, 1990). No diazinon was detected using an LOD of 1.10 µg/L.

USGS Tuolumne River Study. The USGS conducted a study in the Tuolumne River (TR) Basin in California to compare the occurrence, concentrations and mass loading of pesticides in urban and agricultural storm runoff (Kratzer, C.R., 1998). Samples were collected in February 1994-95 during significant storm events after the main pesticide application on dormant almond orchards. There were five storm drains in Modesto, California sampled during the storms, accounting for 47% of the urban area in Modesto with drainage to surface waters. Samples were collected using a width/depth integrated sampling procedure or an auto sampler. The LOD for diazinon was 0.002 µg L⁻¹.

The frequency of detection and concentration of diazinon found in the urban and agricultural storm runoff was related to application. It appears likely that the detections in urban runoff were impacted by agricultural applications (Table 12).

Table 12. Diazinon concentrations ($\mu\text{g L}^{-1}$) in agricultural and urban runoff, Tuolumne River Basin, CA.						
Location	Samples	Detects	Maximum	Median	Mass Load (lbs.)	Sampling Period
Agricultural	8	8	0.920	0.190	1.90	2/6-8/94
Urban	10	10	1.10	0.800	0.18	2/13-14/95

USGS South Platte River Basin Study. A study was conducted by the USGS in the South Platte River Basin of Colorado to compare pesticide contributions from an urban and an agricultural area (Kimbrough and Litke, 1996). The agricultural area was the lower portion of the Lonetree Creek Basin which is mainly irrigated land. Cherry Creek downstream from Cherry Creek Reservoir was used as the urban land-use area. This reach of Cherry Creek flows through mainly urban land and converges with the South Platte River in downtown Denver. Samples were collected using a depth/width integrated method over the period April 1993 to April 1994. The LOD for diazinon was $0.008 \mu\text{g L}^{-1}$. The largest concentrations of diazinon occurred from May through September and after storm events in the urban land-use area (Table 13).

Table 13. Diazinon concentrations ($\mu\text{g L}^{-1}$) in the South Platte River, CO.				
Land Use	Samples	Detects	Range	Median
Urban	25	18	0.450 - ND ¹	0.033
Agricultural	25	6	0.660 - ND	< 0.008

¹ Below the LOD.

NON-AGRICULTURAL USE STUDY SUMMARIES

EPA's Permit Compliance System (PCS) Database. The PCS database stores data for the National Pollutant Discharge Elimination System (NPDES). The Clean Water Act requires that all discharges from any point source, such as a pipe or manmade ditch, into US waters must obtain a NPDES permit. This means that facilities where discharges go directly into surface waters must obtain a permit. This database is accessible via the Internet (http://www.epa.gov/enviro/html/pcs/psc_overview.html).

The PCS database contains surface water samples from 1994 through 1998. The reported LODs range from $20 \mu\text{g/L}$ to $0.01 \mu\text{g/L}$. A search was done for facilities holding NPDES discharge permits for diazinon (raw data are presented in Appendix A). One effluent sample ($638 \mu\text{g/L}$) was not included in the statistical analysis because the concentration seemed high considering that the influent concentration associated with this effluent sample was reported as $10.0 \mu\text{g/L}$.

Diazinon was detected in 52% of the influent samples and 40% of the effluent samples.

Concentrations ranged up to 11.0 µg/L and 10.0 µg/L for the influent and effluent samples, respectively. Mean, median, and 95th percentile concentrations are shown in Table 14.

Table 14. Diazinon concentrations (µg L⁻¹) in POTW influent and effluent in the US (PCS)						
Location	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
Influent	293	153	11.0 - ND ²	0.580	2.00	0.200
Effluent	311	123	10.0 - ND	0.427	1.00	0.178

¹ Range is determined from all samples. Mean, median and 95th percentile are calculated using detects only.

² Below the LOD.

National Effluent Toxicity Assessment Center (NETAC). A nationwide survey was conducted by NETAC to determine the occurrence of diazinon in the effluent from publicly owned treatment works (POTW) (Norberg-King et al., 1989). Samples were collected at POTWs throughout the country, as either 24-hour composite samples or grab samples (raw data in Appendix B). The average LOD for diazinon was 0.081 µg/L with an average recovery of 93%. The raw data are found in Appendix B.

A total of 26 samples were taken; 65% of these contained diazinon residues ranging in concentration up to 0.936 µg/L. Table 15 gives mean, median and 95th percentile values for the detections.

Table 15. Diazinon concentrations (µg L⁻¹) in POTW effluent in the US (NETAC)					
Samples	Detects	Range ¹	Mean	95 th Percentile	Median
26	17	0.936 - ND ²	0.252	0.777	0.159

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

California's Central Contra Costa Sanitary District (CCCSD). A study completed by the California Environmental Protection Agency Department of Pesticide Regulation (DPR) and the Central Contra Costa Sanitary District (CCCSD) in Martinez, California (Singhasemanon et al., 1998) focused on characterizing the diazinon and chlorpyrifos concentrations and mass load in the sewage of residential areas, commercial sites and influent to CCCSD treatment plant. Sampling at five residential areas occurred daily from July 9-15, 1996. Residential areas contribute approximately 82% of the load to the CCCSD treatment plant. Unannounced sampling at twelve commercial sites occurred from July 18 through September 8, 1996. Pet groomers, kennels, and pest control businesses were sampled. Samples were collected at the CCCSD treatment plant from June 22 through September 10 (twice weekly), July 9 - 19 (daily), August 4 -

11 (daily), and August 31 through September 7 (daily), 1996. Samples were also taken daily from the Union Sanitary District (USD) in Alameda County and the Palo Alto Regional Water Quality Control Plant (RWQCP) in Santa Clara County from August 5 - 11, 1996. Samples were collected using programmed auto samplers. The LOD for diazinon was 0.05 µg/L.

Diazinon was detected at nine of twelve commercial sites. The largest diazinon concentration of 20.0 µg/L was detected in the sewage from a kennel (Table 16).

Table 16. Diazinon concentrations (µg L ⁻¹) in sewage and POTW influent, California.							
Location	Samples	Detects	Range ¹	Mean	95 th Percentile	Median	Mass Load (oz)
residential	35	29	4.30 - ND ²	0.408	1.35	0.140	1.48
commercial	32	17	20.0 - ND	2.05	13.4	0.064	0.078
CCCSD	37	37	0.940 - 0.103	0.310	0.702	0.290	NR ³
USD	7	7	0.530 - 0.091	0.239	0.476	0.180	NR
RWQCP	7	7	0.240 - 0.066	0.147	0.225	0.150	NR

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

³ Not reported.

Castro Valley Creek Watershed, CA. A study was conducted during the 1995-96 and 1996-97 rainy seasons (October - May) in the Castro Valley Creek (CVC) watershed (Scanlin and Feng, 1997) to determine the temporal and spatial variability of diazinon in surface water and the sources of diazinon in the watershed. The study area was in west-central Alameda County and contained a mix of residential (50%), commercial (15%) and undeveloped (35%) land. Samples were collected near the mouth of Castro Valley Creek using an autosampler during storm events. Grab samples were also collected during normal flow periods. A mean concentration for each sampled event was determined using a composite sample or calculated from discrete samples. All samples were analyzed using an enzyme linked immunosorbent assay method. The LOD for diazinon was 0.030 µg L⁻¹ (Table 17).

Table 17. Diazinon concentrations (µg L ⁻¹) in Castro Valley Creek, Alameda County, CA.								
Location	Samples	Detects	Range ¹	Mean	95 th Percentile	Median	Mass Load (oz.)	Sampling Period
CVC	19	19	0.820-0.180	0.447	0.766	0.400	22.0	12/4/95-5/17/96
CVC	23	23	0.490-0.035	0.207	0.456	0.170	NR ²	10/4/96-5/21/97

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Not reported.

Diazinon concentrations in CVC appeared to peak in the spring and fall and, therefore, correlated with application patterns. The largest diazinon detections occurred after extended dry periods.

The total mass discharged in the CVC was approximately 0.3% of the total mass applied in the watershed.

Subcatchments in the CVC Watershed were also monitored to determine the spatial variability in diazinon contributions in the watershed. Grab samples were collected at the discharge points of each subcatchment. Samples were collected in April and October of 1996 and February and May of 1997. The subcatchments with the largest areas of undeveloped land had the smallest concentrations (Table 18).

Table 18. Diazinon concentrations ($\mu\text{g L}^{-1}$) in Subcatchments of the Castro Valley Creek Watershed, Alameda County, CA.							
Subcatchment	Samples	Detects	Range ¹	Mean	95 th Percentile	Median	Sampling Period
One	13	10	0.662 - ND ²	0.130	0.492	0.050	4/96 - 5/97
Two	13	11	2.96 - ND	0.380	1.82	0.050	4/96 - 5/97
Three	13	11	0.343 - ND	0.102	0.266	0.069	4/96 - 5/97
Four	13	10	3.40 - ND	0.386	1.84	0.057	4/96 - 5/97
Five	1	1	0.595	NA ³	NA	NA	4/96

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

³ Not applicable.

Samples were collected from 45 randomly selected street gutters during a storm event on May 15, 1996 in residential areas of subcatchments two and three. Two sites with the highest concentrations in the May storm were resampled during a storm in October 1996 with similar results, indicating they may be consistent sources for high diazinon mass loading in the CVC watershed.

Residential Runoff Study in Castro Valley Creek Watershed. A residential runoff study was conducted where diazinon was applied at two residential sites in the CVC Watershed and one in Oakland, CA (14 km from CVC Watershed) in February 1997. Diazinon was applied at two-thirds of the recommended label rate for use on ants as a spray. Grab samples of runoff from roofs, patios and driveways were taken following subsequent rainfall events. Rainfall samples were collected at the Oakland site several days after application. Diazinon was found in all samples collected as long as seven

weeks after application (Table 19).

Table 19. Diazinon concentrations ($\mu\text{g L}^{-1}$) in rainfall and runoff in residential areas of the Castro Valley Creek Watershed, Alameda County, CA.							
Location/Type	Samples	Detects	Range ¹	Mean	95 th Percentile	Median	Sampling Period
Street Gutters	49	45	79.0 - ND ²	4.36	25.5	0.080	5/96 and 11/96
Roof Drains	13	13	17.0 - 0.050	2.19	9.08	0.350	3/97 - 4/97
Patios	6	6	1,200 - 1.40	368	1,120	63.0	3/97 - 4/97
Driveways	3	3	110.0 - 6.00	69.0	107	91.0	3/97 - 4/97
Rainfall	3	3	1.30 - 0.60	0.823	1.26	0.930	3/97

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

Texas Surface-water Quality Monitoring Program (POTWs). A report prepared by the Texas Center for Policy Studies (Kelly et al, 1999) compiled studies related to the quality of drinking water, surface water and ground water in Texas over the last 15 years. The Surface Water Quality Monitoring Program (SWQMP) monitored diazinon in surface water from 1983 to 1997. A total of 151 samples were collected and more than ten of them were above the LOD for diazinon. The LOD was not given. The sampling was random and did not take into account when or where a pesticide was used, rainfall patterns or other factors that could influence the fate of a pesticide in the environment. Diazinon is a problem in POTWs because it is causing them to fail toxicity tests. There are eight large municipal POTWs where this is occurring: Cibolo Creek Municipal Authority, City of Denton, City of Big Spring, City of Greenville, City of Fort Worth, City of Temple, City of Tyler and the Trinity River Authority. Diazinon is not removed during the treatment at these plants.

Florida POTWs (FL DEP). Diazinon use by professional lawn care applicators (approximately 200,000 pounds) is higher in Florida than anywhere else in the US. In Florida, whole effluent testing is done for wastewater treatment facilities; i.e., bioassay testing is done to detect toxicity from a mixture of chemicals, including diazinon. In addition, Florida does not have a water quality standard for diazinon. Concern for diazinon in effluent from these facilities occurred as early as 1988; however, within the past five years the State has recognized an increasing occurrence of diazinon-related toxicity in analyses of effluent. To date, diazinon has been detected in approximately 21 facilities at concentrations ranging from 0.1 to 1.57 $\mu\text{g/L}$. The State of Florida Department of Environmental Protection is now developing a cost effective strategy for analyzing diazinon in wastewater facilities (Williams, 1999, personal communication).

Oklahoma POTWs (OK DEP). Four large wastewater treatment plants have consistently failed toxicity tests from 19 to 19. The Oklahoma Department of

Environmental Quality (DEP) believes that spring and summer lawncare applications are the cause of the diazinon residues in the plants. Because of these failures, USEPA's Region 6 required them to conduct an educational campaign on diazinon use. The DEP now has radio ads and newsletters for the public and also sends the newsletters to Novartis. Oklahoma does not treat for diazinon in their effluent because the only effective method is extremely expensive. The DEP recommends that Novartis be required to put the diazinon toxicity information at the top of their labels and packages in large, bold print to ensure that homeowners understand diazinon's toxicity.

King County, Washington Streams (WA DNR). Urban and suburban streams were tested for diazinon residues in the spring of 1998 by the Washington Department of Natural Resources. Nine out of the 10 streams including Thornton and Longfellow creeks in Seattle; Miller Creek in Normandy Park; Little Soos Creek in Auburn; Sunset, Lewis and Valley Creeks in Bellevue; Juanita Creek in Kirkland; and Lyon Creek in Lake Forest Park contained diazinon ranging from 0.002 to 0.425 µg/L. The contamination is most likely caused by homeowners treating their lawns in the spring. Final study results will be released later in 1999 (Frahm, 1999).

AGRICULTURAL USE STUDY SUMMARIES

Ground water

Missouri. A ground-water monitoring program was conducted to determine the quality of drinking water in agricultural areas (Sievers and Fulhage, 1992). Monitoring was conducted in eight regions considered to be vulnerable to ground-water contamination by pesticides and nitrates based on aquifer material, pesticide use, and agricultural practices. Samples were collected in March, May, September and December from December 1987 to September 1989. A total of 25 wells were sampled in each region. Diazinon was applied to only 2% of the corn grown in Missouri during this time.

Using a method with an LOD of 0.30 µg/L, diazinon was detected in 5 samples at concentrations ranging up to 1.00 µg/L. Four of the five diazinon detections were in a region characterized by glaciated aquifer materials where corn, soybeans, and wheat were the dominant crops. The other detection was in an area dominated by alluvium where corn and soybeans were grown. The average depth to water for the wells where diazinon was detected was 81 feet. There were 354 lbs. a.i. of diazinon applied to corn in six of the monitored regions; diazinon was detected in two of these. Four of the diazinon detections were in December 1987 and one in March 1988 (Table 20).

Table 20. Diazinon concentrations (µg L ⁻¹) in ground water in MO.						
Wells	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
201	804	5	1.00 - ND ²	ND	ND	ND

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the

LOD were given a value one-half the LOD.

² Below the LOD.

Mississippi Pesticide Hazard Assessment Project. From March 1983 to February 1984, 143 shallow (40 - 70 foot) wells were sampled in 10 counties in the Mississippi Delta as part of the Mississippi Pesticide Hazard Assessment Project (Lane, 1987). The counties were chosen because of their high pesticide use and large agricultural production. Using an LOD of 0.01 µg/L (with a recovery of 104 ± 9.23%), seven samples were found to contain diazinon at concentrations ranging up to 0.478 µg/L.

A wood preservative was the most commonly found chemical (70.6% of all detections) suggesting that ground water in these areas may be recharged by water from the Mississippi River (Table 21).

Table 21. Diazinon concentrations (µg L ⁻¹) in shallow wells in the Mississippi Delta.						
Wells	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
143	143	7	0.478 - ND ²	0.013	ND	ND

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

Virginia. A survey of household drinking water supplies from ground-water sources was conducted in Page, Rappahannock and Warren counties during the summers of 1989 and 1990 by the Virginia Cooperative Extension Service (Ross et al, 1991; Ross et al, 1993a,b). All three counties are in rural areas where tree fruits, beef cattle, grains and poultry are the primary agricultural production. The geology of these counties is predominantly shale and limestone with karst topography.

Samples were collected by homeowners as close to the well as possible with one sample collected at each site. The samples were collected from sources that were considered to be high risk based on general water chemistry (nitrate, chloride, etc.) and nearness to activities that could contaminate the water supply (agriculture, etc.). Well depths averaged approximately 200 feet. Using an LOD of 0.01 µg/L, diazinon was detected in 15 wells in two of the counties. Concentrations ranged up to 0.262 µg/L. Samples were analyzed by the pesticide research laboratory at Virginia Technical University (Table 22).

Table 22. Diazinon concentrations (µg L ⁻¹) in household drinking water in VA.							
County	Wells	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
Page	60	60	6	0.103 - ND ²	0.012	0.075	ND
Rappahannock	40	40	9	0.262 - ND	0.023	0.086	ND

Table 22. Diazinon concentrations ($\mu\text{g L}^{-1}$) in household drinking water in VA.							
Warren	26	26	0	NA ³	NA	NA	NA

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

³ Not applicable.

Surface Water

San Joaquin Watershed, CA (DPR). A study is being conducted in the San Joaquin watershed by the California DPR to determine the concentration in surface water of pesticides used during the dormant spray season. Two years of the study have been completed and are reported here (Ganapathy, 1999; Bennett et al., 1998). The sampling locations are located on the San Joaquin River (SJR) near Vernalis and on Orestimba Creek, a western tributary to the SJR. Background samples were collected during the week of December 2, 1996 and December 1, 1997. Dormant season sampling began on January 20, 1997 and January 7, 1998 and continued to March 7, 1997 and March 6, 1998. Samples were collected using a depth/width integrated procedure or single grab samples. Sampling was every other day at the SJR site and twice per week at the Orestimba Creek site. Samples were analyzed by the California Department of Food and Agriculture. The LOD for diazinon was 0.04 $\mu\text{g/L}$ with an average recovery of 92%.

There were no detections of diazinon in the background samples. Dormant spray use of diazinon in the study area (20,573 lbs.) during the winter of 1996-97 was down 58% from the previous winter. The winter of 1996-97 was unusual because rainfall was above average in January 1997, but February was dry. The following year had above average rainfall from January through April. Because of the wet conditions, less diazinon was applied. This may have resulted in reduced concentrations in receiving water bodies. Diazinon detections were correlated with precipitation events and pesticide applications (Table 23).

Table 23. Diazinon concentrations ($\mu\text{g L}^{-1}$) in rivers in the SJR Watershed, CA, Winter 1996-97 and 1997-98.								
Location	Samples	Detects	Range ¹	Mean	95 th Percentile	Median	Mass Load (lbs.)	Sampling Period
SJR	27	10	0.102 - ND ²	0.037	0.091	ND	NR ³	1 - 3/98
SJR	21	3	0.070 - ND	NR	NR	NR	86	1 - 3/97
Orestimba Creek	16	3	0.139 - ND	0.036	0.117	ND	NR	1 - 3/98
Orestimba Creek	16	3	0.092 - ND	NR	NR	NR	7.9	1 - 3/97

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

³ Not reported.

USGS San Joaquin River Basin, CA (SJR). A study was conducted by the USGS (Domagalski, 1997) in the San Joaquin River basin to determine the variability in pesticide concentrations during the irrigation season. The San Joaquin River and selected tributaries were sampled from April to August 1992. There was no rainfall during this period. Samples were collected using width and depth integrated sampling procedures which reduced or eliminated variations in concentrations within the stream channel. The LOD for diazinon was 0.002 µg/L with a recovery between 80 and 100 percent.

Diazinon was detected in almost 100% of the samples taken from the San Joaquin River basin. Concentrations ranged up to 2.00 µg/L (see Table 24 for means, median, and 95th percentile).

A major component of the study was to determine sampling frequency needed to characterize the occurrence and distribution of pesticides in surface water in a semiarid agricultural region such as the SJRB. Results indicated that sampling three times per week is more likely to detect higher concentrations than once per week as indicated by the larger variance about the median for the more frequent sampling. Sampling once per week is sufficient if only the median concentration is important.

Table 24. Diazinon concentrations (µg L⁻¹) in surface water in the SJRB, CA Summer 1992 (USGS)						
Location	Samples	Detects	Range	Mean	95 th Percentile	Median
Orestimba Creek	42	38	2.00 - ND ¹	NR ²	NR	0.052
TID #5	18	18	0.072 - 0.005	NR	NR	0.021
SJR	18	18	0.070 - 0.004	NR	NR	0.008

¹ Below the LOD.

² Not reported.

USGS San Joaquin River Basin, CA (1993). The influence of pesticide and hydrology related variables on the occurrence and concentration of pesticides in surface water in the San Joaquin River (SJR) Basin was explored by the USGS during 1993 (Panshin et al., 1998). Samples were collected at four locations throughout the year at different intervals depending upon the use patterns of the pesticides being monitored as well as precipitation and irrigation timing. Samples were collected using depth/width integrated procedures. The LOD for the study was 0.002 µg L⁻¹ with an average recovery of 102 ± 15% (Table 25).

Diazinon was applied throughout the year and was detected during most of the year. Maximum concentrations were measured in the winter, during the rainy season when diazinon was used on dormant orchards. The sampling location on the SJR, which received flow from the three other sampling locations, was probably not a good location to obtain maximum concentrations of diazinon in the watershed. The SJR site does represent the frequency of occurrence and gives a gross indication of concentrations. Sampling at the subbasin sites is needed if maximum concentrations are to be measured.

Table 25. Diazinon concentrations ($\mu\text{g L}^{-1}$) in the San Joaquin River Basin, CA (USGS).					
Location	Samples	Detects	Range	90 th Percentile	Median
Orestimba Creek	48	34	3.80 - ND ¹	0.560	0.013
Salt Slough	26	23	0.28 - ND	0.160	0.030
Merced River	40	26	2.50 - ND	0.150	0.012
SJR	28	25	0.62 - ND	0.270	0.021

¹ Below the LOD.

San Joaquin River Watershed, CA (Ross). A series of studies were conducted from the spring of 1991 until the winter of 1992-93 in the San Joaquin River (SJR) watershed to determine the distribution and mass loading of insecticides (Ross et al, 1996; Ross, 1993a, 1993b). The samples were collected approximately twice per week at one site (SJR at Laird Park) and at as many as 23 Lagrangian sites over one week periods (sampled daily). The sampling at the Lagrangian sites was triggered by the occurrence of elevated concentrations at the Laird Park site on the SJR. The sampling was timed at the Lagrangian sites so that one parcel of water could be followed through the watershed. Water samples were collected using a width/depth integrated procedure or, when stream conditions were limited, grab samples were collected. The LOD for diazinon was 0.05 $\mu\text{g/L}$ (Table 26).

Peak diazinon concentrations during the dormant spray seasons in 1991-92 and 1992-93 coincided with rainfall events and peak discharges. There were 76,000 and 77,000 lbs. of diazinon applied in the study area during the dormant spray seasons in 1991-92 and 1992-93, respectively. The higher measured diazinon concentrations in the SJR in 1992-93 compared to 1991-92 were a result of the termination of a six-year drought in 1992. There were greater precipitation and larger measured discharges in the SJR in 1992-93. Diazinon oxon was detected at three Lagrangian sites during the winter of 1992-93 (0.70, 0.08 and 0.21 $\mu\text{g L}^{-1}$).

Table 26. Diazinon concentrations ($\mu\text{g L}^{-1}$) in rivers in the SJR Watershed, CA, Winter 1991-92 through Winter 1992-93. (Ross)

Location	Samples	Detects	Range ¹	Mean	95 th Percentile	Median	Sampling Period
SJR	15	13	1.29 - ND ²	0.284	1.25	0.130	12/92-2/93
Lagrangian Sites	44	30	36.8 - ND	1.18	1.69	0.150	1/14-17/93 2/6-10/93
SJR	24	3	0.28 - ND	ND	0.164	ND	7/92-9/92
Lagrangian Sites	36	5	0.32 - ND	ND	0.102	ND	7/27-31/92 8/24-28/92
SJR	21	7	0.10 - ND	ND	0.090	ND	3/92-5/92
Lagrangian Sites	20	2	0.52 - ND	0.052	0.083	ND	4/14-17/92
SJR	17	10	0.35 - ND	0.080	0.182	0.070	12/91-2/92
Lagrangian Sites	36	27	2.14 - ND	0.171	0.488	0.090	1/27-31/92 2/17-19/92

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

USGS San Joaquin-Tulare Basins, CA. The water quality in the San Joaquin-Tulare Basins was monitored over the period 1992-95 by the USGS (Dubrovsky et al., 1998). Transport of diazinon in the SJR was related to timing of diazinon applications and significant precipitation events during the dormant spray season (December-March). Over the period 1991-93, 74% of the diazinon transported in the San Joaquin River occurred in January and February.

San Joaquin, Merced, Tuolumne and Stanislaus River Watersheds (Kratzer). A study was conducted during the winter of 1994 to determine the significance of east-side sources to total diazinon transport in the San Joaquin River (SJR) Basin (Kratzer, 1997). Samples were collected from three tributaries (Merced, Tuolumne and Stanislaus rivers) of the SJR and downstream from the three tributaries. Samples were also collected from two agricultural drains on the Merced River. Sampling occurred throughout two storms in January and February 1994. Dry periods preceded each storm, during which diazinon application occurred. Grab samples or depth/width integrated samples were collected depending on the river conditions. The LOD for the study was $0.002 \mu\text{g L}^{-1}$ with an average recovery of 84%. The diazinon load from each storm represented 0.05% of the total pesticide applied during the previous dry period (Table 27).

Table 27. Diazinon concentrations ($\mu\text{g L}^{-1}$) in surface water in the San Joaquin River Basin, CA. (Kratzer)						
Location	Samples	Detects	Range	median	Mass Load (lbs.)	Sampling Period
Merced River drains	NS ¹	NS	NS	NS	NS	1/23-25/94
	4	4	2.3 - 0.78	1.05	NR ²	2/6-8/94
Merced River ³	3	3	0.61 - 0.30	NR	NR	1/23-25/94
	11	11	0.25 - 0.07	NR	1.5	2/6-8/94
Tuolumne River ³	3	3	2.9 - 0.20	NR	NR	1/23-25/94
	11	11	0.91 - 0.06	NR	1.8	2/6-8/94
Stanislaus River ³	3	3	0.09 - 0.01	NR	NR	1/23-25/94
	11	11	0.08 - 0.01	NR	0.1	2/6-8/94
SJR ³	3	3	0.70 - 0.02	NR	19.6	1/23-25/94
	11	11	0.35 - 0.15	NR	7.8	2/6-8/94

¹ No sample due to insufficient flow.

² Not reported.

³ Range approximated from graphs.

San Joaquin and Sacramento River Watersheds (USGS-CA). The California Regional Water Quality Control Board (RWQCB) and the USGS collaborated on a study to determine the fate of dormant spray pesticides applied in California's Central Valley and transported via surface water to the San Francisco estuary (Kuivila and Foe, 1995). Samples were collected from the Sacramento River (SR), the San Joaquin River (SJR) and two tributaries of the SJR, all of which drain into the estuary. Samples were collected daily (twice daily at Vernalis on the SJR) in January and February 1993 using a depth-integrating, discharge-weighted sampler at either one or three verticals. Diazinon, methidathion, chlorpyrifos and malathion were the focus of this study. The LOD for diazinon was 0.03 $\mu\text{g/L}$. There were field blanks every 20 samples, 10% duplicates and a recovery of greater than or equal to 83% (Table 28).

The frequency of detection and concentration of diazinon in the SR and SJR were related to the timing of storm events and pesticide applications. Diazinon was not found at high concentrations in January in the SR even though there was significant rainfall because application occurred after the major storms. There were elevated levels of diazinon in February in the SR, and in the SJR in both January and February, indicating that significant rainfall events followed pesticide application. The load of diazinon in the SR in January and February was 340 kg and was 98 kg in the SJR. The first pulse of diazinon in February was followed in the SR from Sacramento to the San Francisco estuary. The diazinon concentration at Sacramento was 0.393 $\mu\text{g/L}$; six days later and 119 km downstream it was 0.107 $\mu\text{g/L}$.

Table 28. Diazinon concentrations ($\mu\text{g L}^{-1}$) in surface water in the San Joaquin and Sacramento River Watersheds, CA, Spring 1993.¹ (USGS-CA)						
Location	Samples	Detects	Range ²	Mean	95 th Percentile	Median
SR at Rio Vista	16	16	0.281 - 0.037	0.117	0.260	0.096
SJR at Vernalis	19	19	1.07 - 0.043	0.309	0.830	0.263

¹ Tabular data available only at these sites and for 2/5/93 to 2/25/93 only.

² Range, mean, median and 95th percentile are determined from all samples.

Sacramento River Watershed, 1997-98 (CA-DPR). The California DPR conducted a surface water monitoring study in the Sacramento River (SR) watershed to characterize the occurrence and distribution of organophosphate and carbamate insecticides, including diazinon, and soil applied herbicides that are routinely applied during the winter months (Nordmark, 1998a). Samples were collected at three locations, two on the Sutter Bypass (Karnak and Kirkville) and one on the SR (Alamar). The sampling locations were chosen so as to optimize the sampling of runoff from agricultural areas where dormant spray pesticides are used. Sampling was from January 7, 1998 through March 6, 1998. Background sampling was conducted prior to this during the week of December 1, 1997. Samples were collected using a depth-integrated sampler at two of the sites (Alamar and Karnak) and subsurface grab samples were taken at the third site (Kirkville). Samples were collected every two days on the SR and twice a week on Sutter Bypass. The LOD for diazinon was 0.04 $\mu\text{g/L}$. The average percent recovery for diazinon was 94.7% with a standard deviation of 7.4%. Sample analysis was conducted by the California Department of Food and Agriculture (Table 29).

There were no detections during the background sampling period. Diazinon was detected in every sample but one from January 30 to February 27 in the SR. The period over which the sampling occurred was an unusually high rainfall period, with almost daily measurable rains from the end of December through the end of February. This may have reduced the concentration of diazinon in samples.

Table 29. Diazinon concentrations ($\mu\text{g L}^{-1}$) in the Sacramento River Watershed, CA, Winter 1997-98 (CA-DPR).						
Location	Samples	Detects	Range ¹	Mean	95 th Percentile	Median
SR	27	12	0.170 - ND ²	0.050	0.120	ND
Sutter Bypass	18	6	0.096 - ND	ND	0.090	ND

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

Sacramento River Watershed, 1996-97 (CA DPR, CDFA). A study conducted during the winter of 1996-97 by the California DPR and the California Department of Food and Agriculture (CDFA) (Nordmark et al, 1998b) was a precursor to the above study (Table 29). The sampling locations for Sutter Bypass were the same as in the above study but the sampling location on the SR was at the water intake for the West Sacramento Valley Water Treatment Plant at Bryte. The sampling period was somewhat abbreviated due to flooding in January. Background sampling was conducted during the week of December 2, 1996; sampling continued from January 20, 1997 until the end of the dormant spray season (March 7). During this period, sampling was every other day for the SR and twice weekly at Sutter Bypass. Sampling methodologies and analytical procedures were similar as in the above study. The LOD for diazinon was 0.04 µg/L (Table 30).

Diazinon was not detected during the background sampling period. Diazinon detections during the remaining sampling period were correlated with rainfall events at both locations. Approximate diazinon use in the area was 32% lower than in previous years because of the heavy rainfall in January. There were 52,500 lbs of diazinon applied in January and February 1997, whereas the usage during the same period in 1995 and 1996 averaged 77,000 lbs. Although rainfall was very heavy in January, there was no significant precipitation after January 29. Therefore, the concentrations and mass loading from this study are lower than for a typical dormant spray season.

Table 30. Diazinon concentrations (µg L⁻¹) in the Sacramento River Watershed, CA, Winter 1996-97 (CA-DPR, CDFA).							
Location	Samples	Detects	Range ¹	Mean	95 th Percentile	Median	Mass Load (lbs)
SR	21	4	0.065 - ND ²	ND	0.064	ND	127
Sutter Bypass	14	7	0.086 - ND	ND	0.071	ND	202

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

Sacramento, Merced, Salinas and Russian River Watersheds, CA (Ganapathy).

The Sacramento, Merced, Salinas, and Russian rivers were monitored for one year for organophosphate and carbamate insecticides (Ganapathy et al., 1997). The purpose of the study was to characterize the frequency and concentration of pesticides in runoff from agricultural areas in these watersheds. Samples were collected from one site on each river weekly for one year. Samples were collected with an auto sampler on the SR which resulted in 20 L collected over a period of three days. The auto sampler was used on the Russian and Merced rivers up to January 1995 when heavy flooding occurred. The remaining samples were either depth/width integrated samples or just grab samples when the flow was too high. The samples collected on the Salinas River were either grab or depth/width integrated. Increased sampling frequency (twice/week)

on the Merced River occurred from January 31 through March 6, 1994 to concur with the dormant spray season. Samples were analyzed by the California Department of Food and Agriculture. The LOD for diazinon was 0.05 µg/L with an average recovery of 95% (Table 31).

During the sampling period, 150,011; 3989; 62,000 and 2,220 lbs. of diazinon were applied upstream of the sampling sites in the Sacramento, Merced, Salinas and Russian river watersheds, respectively. Diazinon detections were associated with peak discharge during the rainy season (October - March). The frequency and concentration of diazinon may have been diminished by the three-day sampling composite method as by well as flood events.

Table 31. Diazinon concentrations (µg L⁻¹) in rivers in the Sacramento, Merced, Salinas and Russian River Watersheds, CA, 1993-95 (Ganapathy)							
Location	Samples	Detects	Range ¹	Mean	95 th Percentile	Median	Sampling Period
SR	52	2	0.11 - ND ²	ND	ND	ND	11/93 - 11/94
Merced River	57	3	0.17 - ND	ND	ND	ND	6/94 - 6/95
Salinas River	52	0	NA ³	NA	NA	NA	8/94 - 8/95
Russian River	52	1	0.076 - ND	NA	NA	NA	8/94 - 8/95

¹ Range, mean, median and 95th percentile are determined from all samples. Samples below the LOD were given a value one-half the LOD.

² Below the LOD.

³ Not applicable.

AIR, RAIN AND FOG

Diazinon is the most common organophosphate compound detected in air, rain, and fog (followed by methyl parathion, parathion, malathion, chlorpyrifos, and methidathion). In the 1970's, diazinon was detected throughout the US. Since then, most sampling and analyses have been done in California fog and air.

Air. In 1971, diazinon was detected in approximately 80% of the sites sampled nationally. Over 60% of these sites also contained diazinon OA. By 1988, sampling was done only in California. Diazinon and diazinon OA were detected in approximately 90% and 85% of the sites sampled. A 1976 study indicated that there was a strong correlation between high air concentrations, regional use, and cropping patterns. The primary use of diazinon at that time was in the Corn Belt and Appalachian regions where diazinon was used on corn and tobacco. High diazinon concentrations were also observed in areas where its reported agricultural use was low, possibly indicating the influence of home and garden uses. Concentrations of diazinon in air range from 0.0011 to 306.5 ng/cubic meter; for diazinon-OA they range from 0.0014 to 10.8 ng/cubic meter.

Recent USGS monitoring also indicates that diazinon is being found in Sacramento urban air samples as well as samples taken in agricultural areas upwind and downwind of the urban site. Pesticides can become airborne through volatilization and wind erosion both during and after application. The USGS conducted a study to monitor the occurrence, concentration, and geographical distribution of agricultural pesticides in air over the Mississippi River. The study was conducted from New Orleans, Louisiana to St. Paul, Minnesota during the first 10 days of June 1994. Rainfall was frequent during this period and winds were variable. Herbicides are the most common pesticides used in this area. Each sample was analyzed for 42 pesticides (including 18 insecticides) and 3 degradates; seven insecticides, 16 herbicides, and two degradates were detected. Diazinon was detected in all of the samples (100%) at concentrations ranging from 0.04 to 0.36 ng/m³. Chlorpyrifos, fonofos, malathion, metolachlor, and metribuzin were also detected in 100% of the samples. The highest concentrations of diazinon, chlorpyrifos, and Malathion were observed near major metropolitan areas where agricultural use of these chemicals was minimal.

Recent USGS monitoring indicates that diazinon is being found in Sacramento urban air samples as well as samples taken in agricultural areas upwind and downwind of the urban site (Majewski, 1999, personal communication).

Rain. Concentrations of diazinon in rain ranged from 1.3 to 2,000 ng L⁻¹; for diazinon-OA they ranged from 1.3 to 115.8 ng/L (Majewski and Capel, 1995). More recent monitoring (April-September 1995) has been conducted by the USGS in the Mississippi River valley. Samples were analyzed for 26 herbicides, 18 insecticides, and 3 degradation products in three agricultural/urban regions. Five insecticides, including diazinon, were frequently detected. In two of the three urban sites, significantly more diazinon was detected in the rainfall than at the agricultural sites.

Fog. Of the 48 pesticides that have been detected in fog, only diazinon was near or exceeded the human health limits for drinking water in 5 of 24 fog events (Majewski and Capel, 1995). Concentrations of diazinon in fog were measured as high as 76,300 ng L⁻¹; for diazinon-OA they range up to 28,000 ng L⁻¹.

MODELING

Ground Water

The annual application rate used for diazinon (9.8 lbs. a.i. acre⁻¹) is the maximum recommended value for corn. Table 29 shows the input parameter values used in SCI-GROW (Screening Concentrations in Ground Water) (Barrett, 1997) for diazinon. The K_{oc} value (561 L kg⁻¹) was the average value for all the soil types. This value was chosen because there was a less than a three-fold variation in the K_{oc} values for the soils, indicating that adsorption is correlated with the organic carbon content of the soil. The aerobic soil metabolic half-life (38 days) was the average of two values. The

groundwater concentration resulting from the SCI-GROW modeling is shown in Table 32a. Since there is relatively little temporal variation in ground water compared to surface water, the concentrations can be considered as acute and chronic values.

Table 32a. Input parameters for diazinon used in the SCI-GROW model and result.	
K_{oc} (L kg ⁻¹)	561
Annual Application Rate (lbs. a.i. acre ⁻¹)	9.8
Number of Applications	1
Aerobic Soil Metabolism half-life (days)	38
Groundwater Concentration (µg L ⁻¹)	0.804

Surface Water

Estimated environmental concentrations (EECs) of diazinon in surface water as a result of the highest label application rate on seven crop types (berries, tubers/bulbs, nuts, stone fruits, pome fruits, vegetables and other) were calculated using the Pesticide Root Zone Model version 3.1 (PRZM) (Carsel et al, 1997) and EXAMS 2.97.5 (Exposure Analysis Modeling System) (Burns, 1997). PRZM is used to simulate pesticide transport as a result of runoff and erosion from an agricultural field and EXAMS estimates environmental fate and transport of pesticides in surface water. The weather and agricultural practices are simulated over multiple years (25 or 36) so that the 10-year exceedence probability at the site can be estimated. The crops were chosen based on the uses for which the greatest amount of diazinon was applied according to data from Doanes Marketing Research over the period 1992-1997. PRZM is used to simulate pesticide transport as a result of runoff and erosion from an agricultural field and EXAMS estimates environmental fate and transport of pesticides in surface water. The weather and agricultural practices are simulated over multiple years (25 or 36) so that the ten year exceedence probability at the site can be estimated. A partial list of input parameters for the PRZM/EXAMS modeling are given in Tables 32b and 32c.

Table 32b. PRZM/EXAMS input parameters used for all crops.	
Aqueous Solubility (mg L ⁻¹)	40
Hydrolysis half-life (days) pH 5 pH 7 pH 9	12 138 77
Aqueous Photolysis half-life (days)	no data
Aerobic Soil Metabolism half-life (days)	38
Aerobic Aquatic Metabolism half-life (days)	no data

Table 32b. PRZM/EXAMS input parameters used for all crops.

Source	EFED DERs
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Table 32c. PRZM/EXAMS input parameters for specific crops.

Location/Crop	Major Land Resource Area	Soil Type/Hydrologic Soil Group	Soil/Water Partition Coefficient (K_d) (L kg^{-1})	Annual Application Rate (lbs. a.i. $acre^{-1}$)	Application Method
CA Almonds	17	Kimberlina sandy Loam/B	4.0	1 @ 3.00	Aerial Spray
CA Walnuts	17	Kimberlina Sandy Loam/B	4.0	3 @ 3.00	Aerial Spray
FL Citrus	156A	Adamsville Sand/C	3.7	2 @ 10.0	Aerial Spray
FL Cucumbers	156B	Riviera Sand/C	3.7	1 @ 4.00	Broadcast
FL Strawberries	154	Myakka Fine Sand/B	3.7	4 @ 1.0	Aerial Spray
GA Sweet Corn	133A	Lynchberg Loamy Sand/C	5.0	5 @ 1.25	Aerial Spray
GA Peaches	133A	Boswell Sandy Loam/D	8.0	3 @ 2.0	Aerial Spray
HI Pineapple ¹	NA ²	NA	$K_{oc}=434$	1 @ 4.00	Aerial Spray
LA Sugarcane	131	Sharkey Clay/D	23.4	1 @ 4.00	Aerial Spray
ME Potatoes	143	Conant Silt Loam/D	23.4	1 @ 4.00	Broadcast
MI Blueberries	97	Rimer Loamy Sand/C	5.0	5 @ 1.00	Aerial Spray
MS Cotton	134	Loring Silt Loam/C	23.4	3 @ 1.00	Aerial Spray
MS Soybeans	134	Loring Silt Loam/C	23.4	1 @ 4.00	Aerial Spray
NC Tobacco	133A	Norfolk Loamy Sand/B	5.0	1 @ 3.00	Aerial Spray
NY Apples	144B	Cabot Silt Loam/D	23.4	3 @ 2.0	Aerial Spray
NY Grapes	100	Hornell Silt Loam/D	11.7	5 @ 1.0	Aerial Spray
OR Alfalfa	23	Fury Silt Loam/C	23.4	3 @ 1.5	Aerial Spray
OH Corn	111	Cardington Silt Loam/C	23.4	1 @ 9.80	Aerial Spray
TX Sorghum	77	Pullman Clay Loam/D	23.4	1 @ 4.00	Broadcast
				4 @ 0.50	Aerial Spray

¹ Modeled using GENEEC.² Not applicable.

The standard EXAMS scenario used by EFED simulates a ten-hectare field draining into a one-hectare static pond, that is two meters deep and has no outlet. It is assumed that evaporation losses and inflow from rainfall and runoff are balanced. The aerial

spray application method was modeled assuming an application efficiency of 95 percent with five percent spray drift. The modeling results are shown in Table 32d.

Table 32d. Upper tenth percentile ($\mu\text{g L}^{-1}$) from PRZM/EXAMS modeling.						
Location/Crop	PEAK (ACUTE)	4 DAY	21 DAY	60 DAY	90 DAY	YEARLY AVERAGE (CHRONIC)
CA Almonds	8.89	8.33	7.94	6.39	5.74	1.61
CA Walnuts	21.5	20.7	18.3	16.2	14.5	5.76
FL Citrus	386	365	312	209	160	48.8
FL Cucumbers	429	414	356	258	205	58.7
FL Strawberries	112	109	98.8	83.0	74.8	25.0
GA Sweet Corn	71.1	68.1	57.3	39.0	33.8	11.6
GA Peaches	41.5	40.1	35.2	27.1	22.3	6.61
HI Pineapples	91.2	89.4	80.5	67.2	NA ²	NA
LA Sugarcane	73.4	70.9	62.9	53.1	50.5	13.2
ME Potatoes	72.7	68.7	58.9	45.7	37.0	11.6
MI Blueberries	37.7	36.2	32.8	22.4	19.0	6.47
MS Cotton	40.3	38.1	33.8	26.9	23.1	8.21
MS Soybeans	38.8	37.1	31.2	24.5	20.2	7.15
NC Tobacco	47.0	45.2	38.9	31.7	25.4	7.05
NY Apples	25.1	23.8	20.5	15.4	12.8	4.60
NY Grapes	10.7	10.2	9.10	7.97	7.37	3.33
OH Corn	64.9	62.8	55.2	40.9	34.6	11.2
OR Alfalfa	11.8	11.3	9.78	7.46	6.03	1.81
TX Sorghum	28.8	27.6	23.5	18.8	15.6	5.39



¹ Modeled using GENEEC.

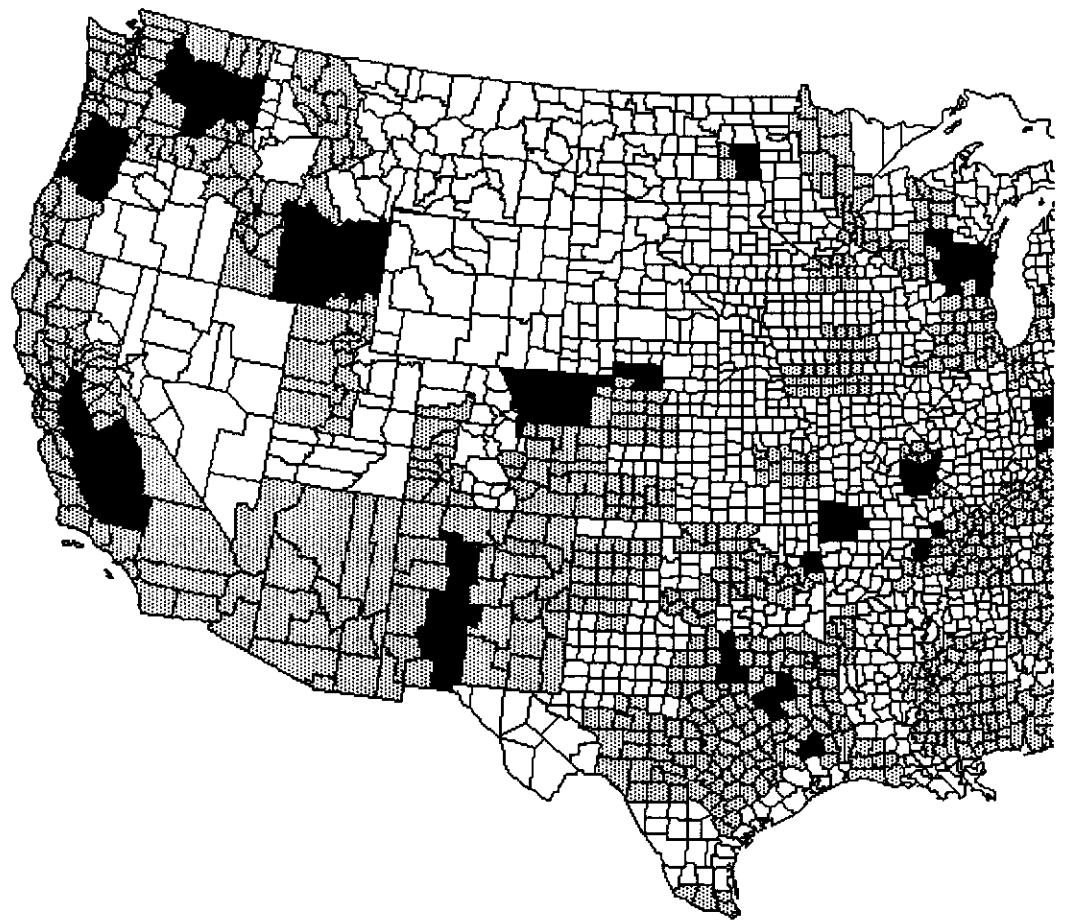
² Not applicable.

There are several factors which may limit the accuracy and precision of the PRZM/EXAMS modeling. These include the selection of the typical exposure scenarios, the quality of the input data, the ability of the models to represent the real world and the number of years that were modeled. The scenarios that are selected for use in Tier II EEC calculations are the ones that are likely to produce large concentrations in the aquatic environment. Each scenario should represent a real site to which the pesticide of concern is likely to be applied. The EEC's in this analysis are accurate only to the extent that the site represents the hypothetical high exposure site. The most limiting part of the site selection is the use of the standard pond with no outlet. A standard pond is used because it provides a basis for comparing pesticides in different regions of the

country on equal terms. The models also have limitations in their ability to represent some processes. The greatest limitation is the handling of spray drift. A second major limitation is the lack of validation at the field level for pesticide runoff.

FIGURE 1. COUNTIES WITH DIAZINON AGRICULTURAL USE AND NAWQA GR

-  COUNTIES WITH AGRICULTURAL DIAZINON USE AND NAWQA GROUNDWAT
-  COUNTIES WITH AGRICULTURAL DIAZINON USE

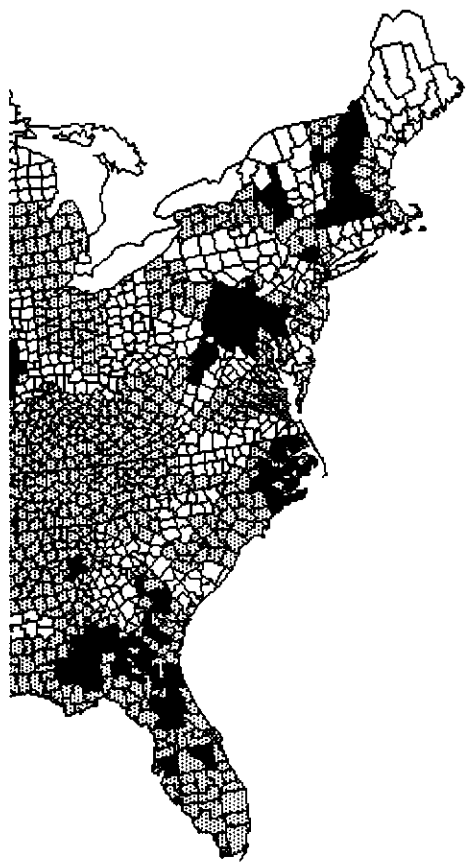


USE DATA FROM USEPA, 1998.

NAWQA SAMPLING LOCATIONS FROM USGS, 1998, NATIONAL WATER QU/
NATIONAL SYNTHESIS PROJECT, [HTTP://WATER.WR.USGS.GOV/PNSP/](http://water.wr.usgs.gov/PNSP/)

GROUNDWATER SAMPLING LOCATIONS



ER SAMPLING LOCATIONS

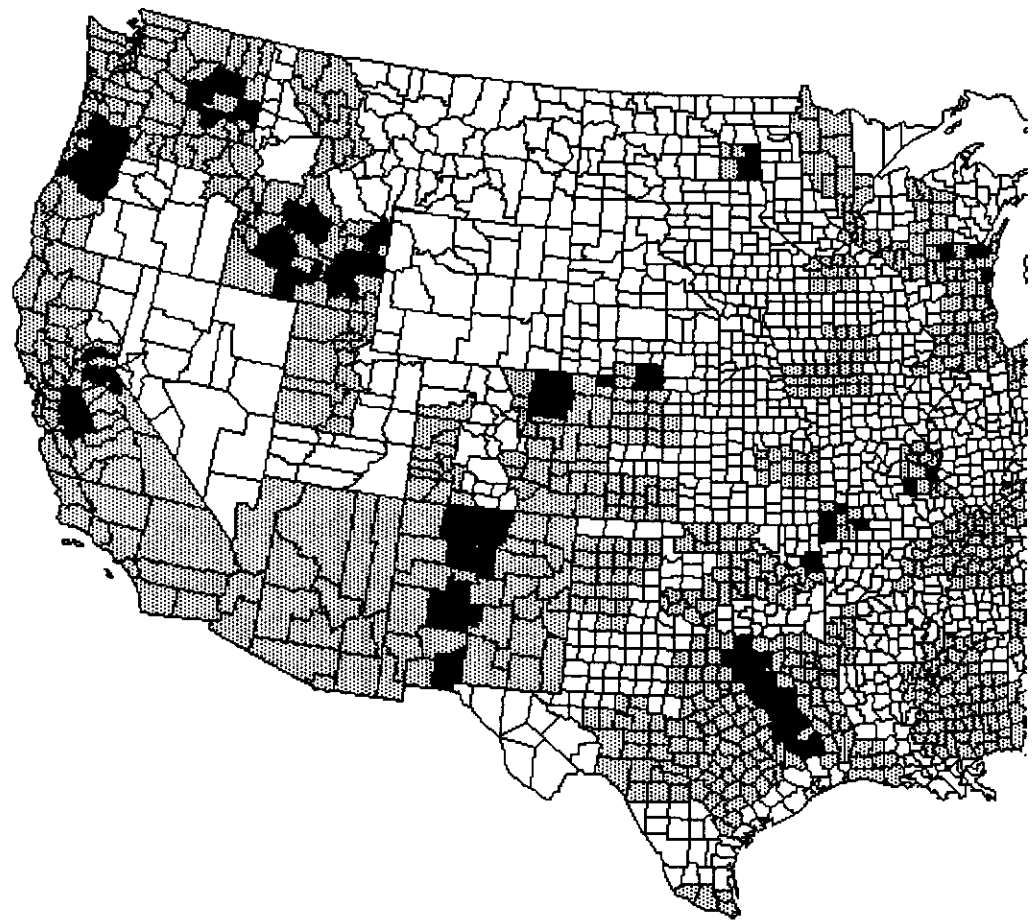


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FIGURE 2. COUNTIES WITH AGRICULTURAL DIAZINON USE AND NAWQA SURFACE WATER SAMPLING LOCATIONS

-  COUNTIES WITH AGRICULTURAL DIAZINON USE AND NAWQA SURFACE WATER SAMPLING LOCATIONS
-  COUNTIES WITH AGRICULTURAL DIAZINON USE

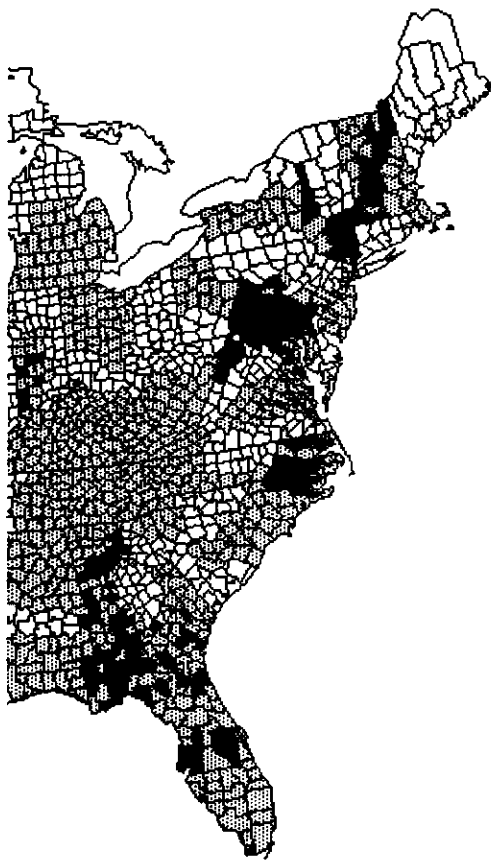


USE DATA FROM USEPA, 1998.

NAWQA SAMPLING LOCATIONS FROM USGS, 1998, NATIONAL WATER QUALITY
NATIONAL SYNTHESIS PROJECT, [HTTP://WATER.WR.USGS.GOV/PNSP/](http://water.wr.usgs.gov/PNSP/)

JRFACE WATER SAMPLING LOCATIONS

VATER SAMPLING LOCATIONS



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